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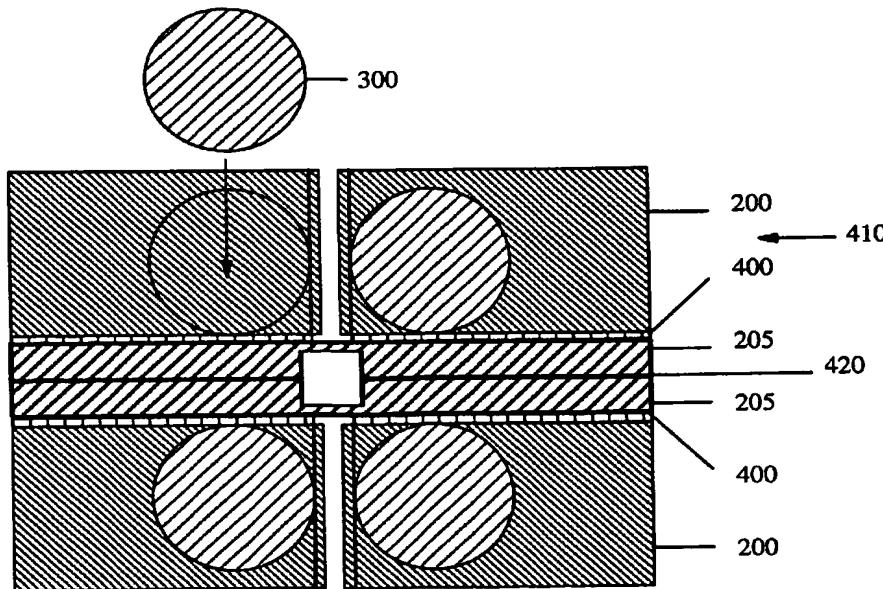
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(54) Title: MONOLITHIC MICRO-ENGINEERED MASS SPECTROMETER



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(57) Abstract: A method of constructing a micro-engineered mass spectrometer from bonded silicon-on-insulator (BSOI) wafers is described with reference to a quadrupole spectrometer. The quadrupole geometry is achieved using two BSOI wafers (200), which are bonded together to form a monolithic block (410). Deep etched features and springs formed in the outer silicon layers are used to locate cylindrical metallic electrode rods (300). The precision of the assembly is determined by a combination of lithography and deep etching, and by the mechanical definition of the bonded silicon layers. Deep etched features formed in the inner silicon layers are used to define ion entrance and ion collection optics. Other features such as fluidic channels may be incorporated.

Title

Monolithic Micro-engineered Mass Spectrometer

Field of the Invention

5 The invention relates to mass spectrometers and in particular to micro-engineered mass spectrometers.

Background to the Invention

10 Mass spectrometers are well known in the art and have particular application in sample measurements. It is also well known to provide miniaturised devices which have particular application as portable measurement systems. The use of such spectrometers is varied from the detection of 15 biological and chemical materials, drugs, explosives and pollutants, to use as instruments for space exploration, as residual gas analysers and as instruments for process control. Mass spectrometers consist of three main subsystems: an ion source, an ion filter, and an ion 20 counter. Since these may all be based on different principles, there is scope for a variety of systems to be constructed.

One of the most successful variants is the quadrupole mass 25 spectrometer, which uses a quadrupole electrostatic lens as a mass filter. Conventional quadrupole lenses such as those described in Batey J.H. "Quadrupole gas analysers" Vacuum 37, 659-668 (1987) consist of four cylindrical electrodes, which are mounted accurately parallel and with their centre-to-centre 30 spacing at a well-defined ratio to their diameter.

Ions are injected into a pupil located between the electrodes, and travel parallel to the electrodes under the influence of a time-varying hyperbolic electrostatic field. 35 This field contains both a direct current (DC) and an

alternating current (AC) component. The frequency of the AC component is fixed, and the ratio of the DC voltage to the AC voltage is also fixed. Studies of the dynamics of an ion in such a field have shown that only ions of a particular charge to mass ratio will transit the quadrupole without discharging against one of the rods. Consequently, the device acts as a mass filter. The ions that successfully exit the filter may be detected. If the DC and AC voltages are ramped together, the detected signal is a spectrum of the different masses that are present in the ion flux. The largest mass that can be detected is determined by the largest voltage that can be applied.

The resolution of a quadrupole filter is determined by two main factors: the number of cycles of alternating voltage experienced by each ion, and the accuracy with which the desired field is created. So that each ion experiences a large enough number of cycles, the ions are injected with a small axial velocity, and a radio frequency (RF) AC component is used. This frequency must clearly be increased as the length of the filter is reduced. In order to create the desired hyperbolic field, highly accurate methods of construction are employed. However, it becomes increasingly difficult to obtain the required precision as the size of the structure is reduced.

The sensitivity and hence the overall performance of a mass spectrometer is also affected by the ion flux, which is also clearly reduced as the size of the entrance pupil is decreased.

Several miniaturised quadrupole mass spectrometers have been constructed. Two examples of such instruments are based on square arrays of miniaturised electrostatic quadrupole lenses and are described in US 5,401,962 and US

5,719,393. The advantage of using an array is that parallel operation can recover the sensitivity lost by miniaturisation. The square array geometry is particularly efficient, because an array of N^2 quadrupoles only requires
5 $(N+1)^2$ electrodes.

The device disclosed in US 5, 401, 962 is commercialised under the brand name "The Ferran Micropole" and is available as a high-pressure residual gas analyser. It
10 consists of a square parallel array of nine quadrupole analysers constructed using sixteen cylindrical metal rods 1 mm in diameter and 20 mm long, mounted in miniature glass-to-metal seals. The ion source is a conventional hot-cathode device. The quadrupoles are driven in parallel by a
15 RF generator, and the ion detector consists of an array of nine Faraday collectors connected together.

The array-type quadrupole mass spectrometer described in US 5, 719, 393 was developed by the Jet Propulsion Laboratory
20 (JPL) and has electrodes that are welded to metallised ceramic jigs. The ioniser is a miniature Nier type design with an iridium-tungsten filament. The detector can be a Faraday cup or a channel-type multiplier.

25 Quadrupole lens arrays smaller than the devices described above have been fabricated by exposing a photoresist to synchrotron radiation and then filling the resulting mould with nickel by electroplating, in a collaboration between JPL and Brookhaven National Laboratory and described in US
30 6, 188, 067. The lens assembly is a planar element, which is configured into a stacked structure in the complete mass spectrometer. However, there is no evidence of successful operation of the device.

A different micro-engineered quadrupole lens has been developed jointly by Imperial College and Liverpool University, and is described in US 6, 025, 591. The device 100, as shown in Figure 1, consists of four cylindrical electrodes 115 mounted in pairs on two oxidised, silicon substrates 105, that are held apart by two cylindrical spacers 120. V-shaped grooves 110 formed by anisotropic wet chemical etching are used to locate the electrodes and the spacers. The electrodes are metal-coated glass rods that 10 are soldered to metal films 125 deposited in the grooves.

The mounting method is similar to that used to hold single-mode optical fibres in precision ribbon fibre connectors. In each case, positioning accuracy is achieved by the use 15 of photolithography followed by etching along crystal planes to create kinematic mounts for cylindrical components. However, in the quadrupole lens, the two halves of the structure are also self-aligning. The degree of miniaturisation is only moderate, and operation has been 20 demonstrated using devices with electrodes of 0.5 mm diameter and 30 mm length. Wirebond connectors 135 are used to provide for electrical contact to the components of the device.

25 Although mass filtering has been demonstrated, the method of fabrication has some disadvantages. The electrode rods require lengthy cutting, polishing and metallisation. Because the electrodes must be metal-coated everywhere, 30 metallisation involves multiple cycles of vacuum deposition. The bonding process used to attach the electrode rods is a time consuming manual operation, requiring axial alignment. Additional fixtures are needed, to hold the assembly together, and there is no axial alignment of the two substrates, which may slide over each 35 other.

The method of fabrication also results in some important performance limitations. The oxide layer is electrically leaky, so that the drive voltage (and thus the mass range) 5 is limited. As a result, current device performance is insufficient for applications requiring measurement of large masses (e.g. drugs or explosives detection).

There is also significant capacitance coupling to the 10 resistive substrate, which rises as the RF frequency is increased. The device therefore forms a poor RF load, and the mass selectivity is limited. Resistance heating in the substrate also tends to melt the solder, causing the rods tend to detach from the V-grooves.

15 In addition, the construction forms only a mass filter, and an ion source and detector must also be added to form a complete mass spectrometer. These elements require components for creation and detection of ions, and also for 20 accelerating and focusing ions.

There is therefore a need to provide an improved mass spectrometer device, which can be easily fabricated. There 25 is a further need to provide an array-type device, which could be used to increase the currently low instrument sensitivity.

Object of the Invention

It is an object of the present invention to provide an 30 improved mass spectrometer.

Summary of the Invention

Accordingly the present invention provides an integrated 35 mass spectrometer device. In a wafer-scale batch

fabrication process, a plurality of similar dies are formed on two multilayer wafers, each wafer having an inner layer, an outer layer and having an insulating layer provided therebetween. Alternatively, in a small-scale fabrication 5 process, a single device is formed from two dies taken from a single multilayer wafer. The two approaches are similar and in the following description "die" may be substituted for "wafer" without alteration of the general meaning. The device is provided with a plurality of electrode rods and a 10 plurality of electrodes, the electrodes and electrode rods being formed on distinct layers of the wafers.

The spectrometer is desirably a quadropole mass spectrometer and the invention additionally provides a 15 method of constructing such a micro-engineered quadrupole mass spectrometer, which overcomes many of the difficulties associated with the above prior art. Such a quadropole device requires at least four electrode rods, typically cylindrical with each rod having its diameter and centre- 20 to-centre separation correctly chosen for quadrupole operation.

The horizontal separation of the cylindrical electrodes within each wafer is desirably defined by lithography and 25 deep reactive ion etching.

The vertical separation of the cylindrical electrodes is typically defined by the combined thickness of the two inner layers, which are bonded together during the 30 fabrication process.

Ignoring additional coatings, each of the multilayer wafers desirably has three layers, which are combined to form a five-layer structure.

The electrode rods preferably are mountable in the outer layers of each wafer. Desirably the rods are cylindrical electrode rods and are made from metal, thus simplifying electrode preparation.

5

The outer layers of each wafer are suitably dimensioned to receive the electrode rods therein, the electrode rods being retained in contact with the outer layer by the provision of at least one resilient member formed in the outer layer. Such retention is desirably provided by mounting the electrode rods in etched slots within the wafers and retaining them therein using silicon springs, thus simplifying assembly, avoiding the need for bonding material, and reducing the likelihood of detachment. The slots and springs are typically etched in bonded silicon-on-insulator substrates, using deep reactive ion etching. The precision of the assembly is determined by a combination of lithography and deep etching, and by the mechanical definition of the bonded silicon layers.

20

Each of the first and second wafers is typically patterned with an outer pattern on a first side, and an inner pattern on a second side. The use of both sides of each wafer is thereby enabled.

25

The patterns provided on the second side typically provide for ion source and ion collection components of the spectrometer, which may be used together with components for accelerating, focusing or reflecting the ions

30

The insulating layer is desirably provided in regions where the patterns overlap.

35

The first and second wafers are typically bonded to form a monolithic block. The bonding is desirably effected in such

a manner that the electrode rods are located on an outer portion of the block and the electrodes in an inner portion of the block.

- 5 At least some of the plurality of electrodes are desirably adapted to form ion entrance optics. These ion entrance optics are typically formed by an einzel lens.

At least some of the plurality of electrodes are desirably
10 adapted to form ion exit optics. These ion exit optics may also be operated in a mode that reflects a desired fraction of ions, thus enabling operation as a linear quadrupole ion trap such as that described in WO 97/47025 in addition to operation as a linear quadrupole mass filter.

- 15 One of the plurality of electrodes may in addition be adapted to form an ion collector.

A hot cathode electron source may be provided in front of the ion entrance optics for the purpose of ion creation by
20 electron impact. In another embodiment, a cold cathode field emission electron source may be provided in front of the ion entrance optics for a similar purpose. It will be understood that the choice of electron source used will typically be determined on the basis of the type of ion
25 fragmentation required and that some types of sources may be chosen as being more appropriate for one type of fragmentation than other types.

In another embodiment, a pair of RF electrodes is placed in
30 front of the ion entrance optics in order to create a plasma from which ions may be extracted.

In a further embodiment, a pair of electrodes is placed in front of the ion entrance optics and used with DC voltages
35 in order to create a glow or corona discharge from which

ions may be extracted.

In a further embodiment, the ion entrance optics are formed from an etched fluid channel combined with a set of 5 electrodes that together define an electrospray source of ions.

Two or more devices may be combined to form an array which may be formed either as a plurality of devices formed in 10 parallel or in series. When arranged in parallel, it will be appreciated that the array forms multiple quadrupole filters having greater total ion throughput and greater measurement accuracy. When arranged in series, the array forms a tandem mass spectrometer, having more complex 15 measurement possibilities. This configuration may include a pair of electrodes provided between each pair of the devices in the series so as to form a plasma

The invention additionally provides a method of forming a 20 mass spectrometer comprising the steps of:
etching an inner and outer pattern on a wafer, the inner and outer patterns defining components for the spectrometer,
bonding the wafer to a second wafer so as to form a 25 multilayer stack device,
inserting at least one electrode rod into the device. The at least one electrode and one electrode rod are desirably formed on distinct layers of the wafer.

30 It will be appreciated that the quadrupole geometry is achieved using two substrates, which are aligned and bonded into a single block using a bonding tool. The formation of a monolithic block increases the rigidity and reliability of the device. No additional components are required to 35 align the structure or hold it together. The mounting of

- electrodes on the outside of the two substrates ensures that it is easier to access and position the electrodes. Electrical isolation is desirably provided by thick layer of high quality silicon dioxide, thus minimising leakage
- 5 and maximising the voltage that can be applied. The majority of the silicon around the rods is typically removed, thus minimising capacitance coupling and maximising the usable frequency.
- 10 Ion coupling optics and other features such as fluidic channels may be incorporated in the structure. Because the electrodes are located on the outside of the block, it is simple to construct an array device. Cascaded devices such as tandem mass spectrometers may be constructed in a
- 15 similar way.

These and other features of the present invention will be better understood with reference to the drawings and description thereof which follow.

20

Brief Description of the Drawings

- Figure 1 shows a prior art micro-engineered quadrupole electrostatic lens,
- 25 Figure 2 is a plan view showing a) the outer and b) the inner etched patterns in a monolithic, micro-engineered mass spectrometer according to the present invention,
- Figure 3 is a plan view showing a) the registration of the outer and inner pattern, and b) the location of the
- 30 electrode rods by the outer pattern in a device according to the present invention,
- Figure 4 is a cross-sectional view, showing a) wafer bonding and b) electrode rod insertion of the device of Figure 3,

Figure 5 is a simplified flow chart showing the fabrication steps involved in the construction of a monolithic, microengineered mass spectrometer according to the present invention,

5 Figure 6 is a schematic illustrating electrical connections to a monolithic, micro-engineered mass spectrometer according to the present invention,

Figure 7 is a schematic showing the location of a) a cold cathode field emission electron source, b) an RF plasma

10 source and c) an electrospray source at the input to a monolithic, micro-engineered mass spectrometer according to preferred embodiments of the present invention, and

Figure 8 is a schematic showing the location of a collision chamber between cascaded quadrupole lenses, as required in 15 tandem mass spectrometry.

Figures 9a and 9b shows the assembly of two etched parts to form an electrostatic element based on apertures and on apertures covered by one-dimensional meshes.

Figures 10a, 10b and 10c show plan views of the pattern 20 required on one substrate to construct three-element electrostatic lenses, using different combinations of apertures, tubes and meshes.

Figures 11a and 11b show plan views of hot-cathode ion sources constructed using external and integrated 25 filaments.

Detailed Description of the Drawings

Figure 1 has been described with reference to the prior 30 art.

The present invention will now be described initially with reference to Figures 2 - 6, which show an example of a new method of construction, based on deep-etched features 35 formed in bonded silicon-on-insulator (BSOI) material,

according to a preferred embodiment of the invention. BSOI consists of an oxidised silicon wafer, to which a second silicon wafer has been bonded. The second wafer may be polished back to the desired thickness, to leave a silicon-
5 oxide-silicon multi-layer. BSOI wafers typically find application in high-voltage microelectronics. However, the different layers in the wafer may also be processed using semiconductor microfabrication techniques to yield a three-dimensional structure. Further embodiments or modifications
10 are illustrated with reference to Figures 7 to 11.

In accordance with the present invention two BSOI wafers are required, each with a double-side polish. Alternatively, two dies from the same wafer may be used in
15 a small-scale process. Figure 2 shows how each wafer may be patterned with an outer pattern on the first side 200 (Figure 2a) (the original substrate wafer side), and an inner pattern on the second side 205 (Figure 2b) (the bonded wafer side). The features are desirably made by deep
20 reactive ion etching (DRIE), a process used to form near vertical trenches with very high precision.

The pattern is transferred into the silicon from a shallower surface mask layer, which is resistant to the reactive species commonly employed in deep reactive ion etching. Suitable mask materials are thick layers of hard-baked photoresist and silicon dioxide. The first steps of processing therefore involve deposition and patterning of
25 the mask layers. Photoresist may be spin-coated and patterned by photolithography. Silicon dioxide may be formed by thermal oxidation or coated by chemical vapour deposition. It can be patterned by reactive ion etching,
30 using a thinner layer of photoresist as a mask.

There is considerable flexibility in the patterns that may be used. The following description, with reference to Figure 2 to 6, corresponds to an exemplary embodiment that illustrates the advantages of the constructional approach provided by the present invention and the differences from the prior art previously described, and it will be appreciated by those skilled in the art that modifications to the specific pattern described may be effected without departing from the scope of the invention. Further aspects are illustrated in Figures 7 - 11.

Figure 2a shows a plan view of the outer pattern 200. This pattern is adapted to provide for the retention of electrodes and in this illustrated embodiment consists of a set of locating features 210, 215 for two cylindrical electrode rods (not shown), and two flexible members which are shown as springs 220, 225 to retain the rods in place. The rod diameters are comparable to the thickness of the wafer.

Figure 2b shows a plan view of the inner pattern 205. At the left-hand end, this pattern consists of a set of three electrodes 230, 235, 240 that can act as an einzel lens, a common electrostatic optical component that is used to focus charged particles into an electron or ion optical system. At the right-hand end, this pattern consists of a similar (but not identical) set of two electrodes 245, 250 that can act as a Faraday cage and an ion collector at the exit of the system. In effect, the first and second sets of electrodes form the ion source and ion counter - the entrance and exit optic pupil components of the spectrometer device.

The patterns may be etched through the entire thickness of the bonded layer. Alternatively, more complicated

processing involving two mask layers may be used to limit the depth of the pattern in some areas. For example, a small thickness of the silicon may be left linking the upper and lower electrodes in the einzel lens and the 5 Faraday cage, as shown by the fine shading 255 in Figure 2b. It will be appreciated that this process may be achieved using a number of different techniques such as delayed shadow masking. Certain other techniques provide for some parts of the electrode pattern to be continued 10 into the layers beneath.

Figure 3a shows the relationship of the outer and inner patterns. In some areas, additional features are added to the outer pattern to ensure mechanical continuity between 15 the two layers, so that the overall structure is rigid. In other areas, the outer layer pattern is cut away, so that all the electrodes may be accessed from the outer side of the structure. The two patterns may be registered together with high accuracy using a double-side mask aligner.

20 Figure 3b shows the eventual location of cylindrical electrode rods 300 within the outer layer pattern. The locating springs 220, 225 hold the two rods so that they are symmetrically displaced on either side of an optical 25 axis defined by the entrance and exit optic pupils formed by the patterns on the inner layer. The springs also make electrical contact to the electrode rods.

As shown in the sectional view of Figure 4a, an oxide 30 interlayer or insulating layer 400 is provided between the inner and outer layers of each wafer. After deep reactive ion etching, the oxide interlayer is partially removed by wet chemical etching, to leave oxide remaining only in the regions where the patterns in the inner and outer layers 35 overlap. It will be appreciated that certain applications

may require the addition of additional oxide insulation to be provided over the structure by thermal oxidation, or by a coating process such as chemical vapour deposition.

Further processing is then used to provide metal contacts to each silicon electrode in the entrance and exit optical system, and to the silicon springs that retain the cylindrical electrodes. Because the contacts may all be accessed from the outer layer of the structure, this metal may be added by single-sided vacuum deposition.

Alternatively, a conformal coating process such as sputter deposition may be used to provide a metal coating to all the silicon parts.

Once each of the two wafers has been patterned they may be aligned together and bonded. Ignoring additional coatings such as metals, this process will leave a silicon-oxide-silicon-oxide-silicon multilayer stack 410, as shown in the cross-sectional view of Figure 4a. It will be appreciated that each wafer comprises three layers; the outer and inner layers and an isolation layer provided therebetween. In the bonding process each of the inner layers are integrally bonded to form a bond interface 420, such that in the complete stack only five distinct layers are present. It will be understood that the five distinct layer arrangement just described does not include the additional coatings that may be present on each or one of the individual layers making up the stack. The alignment and bonding may be carried out using a variety of techniques such as a bonding tool equipped with a microscope and mechanisms for compression and heating. Additional bonding agents such as solder materials may also be used. The resulting composite wafer is then diced to separate the individual dies. At this stage, each device is a single rigid, monolithic block. Each device is then attached to a submount, and wirebond connections are made to the contact metallisation.

Metallic electrodes 300, desirably cylindrical, are then inserted into the block 410 from the outside, as shown in the cross-sectional view of Figure 4b. In the example of a 5 quadrupole spectrometer, four electrodes are utilised and the four electrodes have their diameters and centre-to-centre separations chosen for quadrupole operation. The horizontal position of each electrode is defined by the 10 locating features and springs etched into the outer layer pattern. The vertical separation of the electrodes is defined by the thickness of the two inner bonded silicon layers, which may be accurately specified in commercially available BSOI material.

15 The fabrication process above is summarised in Figure 5. This figure shows the steps of (1) depositing a mask layer on the first and second sides of a wafer; (2) patterning the mask layer on the first and second sides; (3) deep reactive ion etching of the first and second sides of the 20 wafer; (4) removal of residual portions of the mask layer; (5) wet etching of the oxide interlayer; (6) metallisation of the first side or both sides of the wafer; (7) bonding of two wafers into a two-wafer stack; (8) dicing of the resulting composite wafer; (9) mounting and wirebonding of 25 individual dies, and (10) insertion of cylindrical electrode rods. It will be understood that variations in the process steps or the order of their use may also achieve a similar result, and it is not intended to limit the present invention to any one sequential set of steps.

30 Electrical connections to the device are made as shown in Figure 6. DC voltages V_1 , V_2 and V_3 are applied to the einzel lens electrodes and V_4 to the Faraday cage. Voltages V_{RF1} and V_{RF2} containing both a DC and an AC component are 35 applied to the cylindrical electrodes. The DC and AC

components have the ratios commonly used in quadrupole mass spectrometers to provide mass filtering. The ion current I is collected from the electrode to the right of the Faraday cage and passed to a transimpedance amplifier (not shown).

5

In an alternative configuration, the integrated ion collector may be omitted and an external detector such as a channel-type multiplier may be used.

- 10 The electrodes provided in the description above are suitable for coupling an ion flux into the quadrupole assembly, performing a mass filtering operation, and detecting the resulting filtered stream of ions. Further components are required to create the ion flux. Figures 7a
15 and 7b show modifications to the previous structure so as to optimise the performance for gaseous analytes. Figure 7c shows a modification appropriate for liquid analytes,

20 For a gaseous analyte, ionisation may be carried out by electron bombardment. A suitable electron stream may be provided by a cold-cathode field emission electron source, fabricated as a planar array of Spindt emitters 700. The source may be located (for example, by hybrid integration) on an etched silicon terrace, immediately in front of the
25 ion input coupling optics as shown in Figure 7a. The source is arranged to emit electrons in a direction perpendicular to the main axis of the mass spectrometer, so that the electron and ion streams may be efficiently separated.

- 30 Alternatively, the electron source may be located outside the device, and electrons may be injected through a mesh-shaped or alternatively shaped or dimensioned opening. An advantage of a mesh-shape is that this configuration allows the ions to be created within an equipotential source cage.

Alternatively, ionisation may be carried out within a gas plasma, which itself may be created by an RF electric field 705, as shown in Figure 7b. The field may be established between a pair of electrodes located on etched silicon 5 terraces, located immediately in front of the ion input coupling optics. Again, the RF field is arranged to accelerate electrons in a direction perpendicular to the main axis of the mass spectrometer, so that the electron and ion streams may be efficiently separated.

10

Alternatively, ionisation may be carried out within a DC discharge, which may be created by a similar pair of electrodes carrying DC potentials.

15

A relatively high pressure is required to sustain a plasma or a DC discharge. This pressure is not normally compatible with mass filter operation, since the mean free path is too short. However, the ability to create sealed or partly sealed chambers by bonding two wafers as described in this 20 invention allows the construction of a differentially pumped system, in which the source chamber operates at high pressure and the mass filter at low pressure.

25

For a liquid analyte (for example, as provided by a liquid chromatography column), ionisation may be carried out within an electrospray source. A suitable source may be constructed by using an etched capillary channel 710 located immediately in front of the ion input coupling optics as shown in Figure 7c. Liquid may be extracted from 30 such a channel as a stream of charged droplets by a nearby electrode held at a sufficiently large DC potential.

35

It will be appreciated by those skilled in the art that all of the above may be implemented using the process described in Figure 5, or by modifications thereto that either

involve simple alterations to the layout of the etched structures, or that require additional steps of metal and oxide deposition, patterning and etching.

5 It will be appreciated that although it has been described with reference to the formation of distinct devices that the fabrication approach described above (namely, the use of patterning, deposition and etching to create a number of similar structures on a semiconductor wafer) may clearly be
10 extended to create parallel arrays of devices in close proximity, which may act as an array-type mass spectrometer. The quadrupole lenses may be driven in parallel, and the ion currents summed, to obtain an increase in instrument sensitivity. Alternatively, the
15 quadrupole lenses may be driven separately, and the ion currents measured separately, to obtain a separate measure of a number of different ion species.

The fabrication approach described above may also be
20 extended to create serial arrays of devices in close proximity, which may provide advanced functionality. For example, Figure 8 shows two quadrupole lenses 800, 805, which are connected in series to act as a tandem mass spectrometer. The first quadrupole 800 may be set to pass
25 only those ions that have masses in a particular range, thus acting as a prefilter. The selected ions may be fragmented in a collision chamber 810, and passed to the second quadrupole 805 for further analysis.

30 The collision chamber 810 is desirably a small volume within which a plasma may be created by excitation of an inert gas (for example, argon) using a pair of RF electrodes 815. The construction of a collision chamber using the methods described above merely involves
35 additional steps of metal and oxide deposition, patterning

and etching. Differential pumping may again be employed to allow this chamber to operate at a higher pressure than the quadrupole filters. These additional steps will be apparent to those skilled in the art.

5

It will be understood that the formation or provision of complex electrodes and/or electrostatic elements may require specific multi-level processing such as that provided by multiple surface mask layers. In such techniques, two or more masks are used in combination with one another to provide for a complex patterning of the base silicon material so as to provide the desired physical configurations.

15 Figure 9a shows how such multilevel features may be used to construct an electrode suitable for controlling charged particles such as ions or electrons. Two wafers 900, 905 (or alternatively two dies) are shown, and the complete electrode 910 is constructed by bonding the two wafers 20 together. The features that have been partially etched combine to yield an aperture 915 formed in a planar diaphragm electrode 920 defined by the fully etched features. Figure 9b shows how this concept may be extended to form an electrode 925 consisting of an aperture covered 25 by a one-dimensional mesh 930. In this case, the first mask layer must be patterned to leave a set of closely spaced, strips in the vicinity of the aperture.

30

Electrode structures formed in this way may be used to construct a variety of lens elements and electrostatic devices. For example, three apertured diaphragms 1000 may be used to form an einzel lens, as shown in Figure 10a. Alternatively, the central diaphragm may be replaced by a mesh 1010 as shown in Figure 10b. This configuration allows 35 stronger focusing or stronger reflection. Finally, any or

all of the three electrodes may be extended axially to form a tube 1020 with a rectangular or square cross-section, as shown in Figure 10c.

- 5 The last configuration is particularly advantageous in a quadrupole device as described in the present invention. Near the entrance and exit of the quadrupole lens, the electric field is distorted by the presence of nearby structures used to support and locate the cylindrical
10 10 electrode rods. A tube-shaped electrode may advantageously be employed at either end of the quadrupole to shield the ions from these field imperfections.

Figure 11 shows further uses of multilevel processing to
15 form components of a mass spectrometer system. In Figure 11a, a mesh element 1100 is used to define part of the perimeter 1110 of a source cage 1120 into which electrons are injected from an external filament 1130. In Figure 11b, a similar structure containing an integrated filament 1140
20 which is also formed by etching. In another configuration, a removable filament formed by etching may be used. It will be appreciated that there are many other possible arrangements of such structures, and these examples are not exhaustive.

25

As mentioned above, at least some of the plurality of electrodes may be adapted to form ion exit or entrance optics adapted to operate in a mode that reflects a desired fraction of ions. Such a configuration of ion reflectors
30 may be used to provide an ion trap.

In operation, ions would be introduced into the mass filter portion of the spectrometer, and then by reversing the voltages applied to entrance or exit optics, the ion within
35 the filter would be continually reflected up and down the

filter, thereby being trapped and further filtered until the voltages applied to the optics were changed to enable the ions to escape from the trap or until the ions escape by virtue of energy acquired from the filter itself.

5

It will be understood that the arrangement of electrodes at both the entrance and exit of the mass filter portion can be configured in one of a plurality of different arrangements. For example, a three electrode structure

10

could be provided in which the two outer elements are provided with the same voltage. In such an arrangement, an ion will have substantially the same potential on either side of the lens so that the system operates predominately in a single-potential fashion. Such arrangements are

15

typically known as einzel lens arrangements. In other arrangements different numbers of electrodes could be provided so as to provide alternative lens structures or configurations. It will be understood that the number of electrodes or voltages applied to individual electrodes may differ, depending on the application to which the system is being applied, and it is not intended to limit the present invention to any one arrangement.

25

The present invention provides a mass spectrometer that is advantageous over prior art devices. Utilising a device according to the present invention it is possible to provide for more complex mass analysis than was heretofore possible by cascading filters, typically quadrupole filters. The device of the present invention is also advantageous in that it enables the connection of a quadrupole filter to fluidic devices containing etched channels, such as in a gas or liquid chromatography system (for example, as in a gas chromatograph mass spectrometer or GC-MS system), so as to extend the range of applications of such devices.

The words "comprises/comprising" and the words "having/including" when used herein with reference to the present invention are used to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. Similarly the words "upper", "lower", "right hand side", "left hand side" as used herein are for convenience of explanation and are not intended to limit the application of the device or technique of the present invention to any one specific configuration.

Claims

1. An integrated mass spectrometer device formed from two multilayer wafers, each wafer having an inner layer, an outer layer and having an insulating layer provided therebetween, the device having a plurality of electrode rods and a plurality of electrodes, the electrodes and electrode rods being formed on distinct layers of the wafers.
- 10 2. The device as claimed in claim 1 wherein each of the multilayer wafers has at least three layers which are combined to form a five layer structure.
- 15 3. The device as claimed in claim 1 or 2 wherein the electrode rods are mountable in the outer layers of each wafer.
- 20 4. The device as claimed in claim 3 wherein the outer layers of each wafer are dimensioned to receive the electrode rods therein, the electrode rods being retained in contact with the outer layer by the provision of at least one resilient member formed in the outer layer.
- 25 5. The device as claimed in claim 4 wherein the at least one resilient member is provided by a spring formed in the wafer.
- 30 6. The device as claimed in claim 4 wherein the electrode rods are located by etched features in the outer layer of the wafer, the features being dimensioned so as to suitably receive a rod, and wherein the resilient members is formed by also etching the outer layer.
- 35 7. The device as claimed in any preceding claim wherein each

of the first and second wafers are patterned with an outer pattern on a first side, and an inner pattern on a second side.

5 8. The device as claimed in claim 7 wherein the patterns provided on the second side provides for ion source and ion collection components of the spectrometer.

10 9. The device as claimed in claim 7 or 8 wherein the insulating layer is provided in regions where the patterns overlap.

15 10. The device as claimed in any preceding claim wherein the first and second wafers or individual dies therefrom are bonded to form a monolithic block.

20 11. The device as claimed in claim 10 wherein the bonding of the first and second wafers is effected such that the electrode rods are located on an outer portion of the block and the electrodes in an inner portion of the block.

25 12. The device as claimed in any preceding claim wherein the electrode rods form a mass filter component of the mass spectrometer.

30 13. The device as claimed in claim 12 including four cylindrical electrode rods, each rod having its diameter and centre-to-centre separation correctly chosen for quadrupole operation.

35 14. The device as claimed in claim 12 or 13 wherein the horizontal separation of the cylindrical electrodes within each wafer is defined by lithography and deep reactive ion etching.

15. The device as claimed in any one of claims 12 to 15
wherein the vertical separation of the cylindrical
electrodes is defined by the combined thickness of the
5 two inner layers, which are bonded together during
assembly.
16. The device as claimed in any preceding claim wherein at
least some of the plurality of electrodes are adapted to
10 form ion entrance optics.
17. The device as claimed in claim 16 wherein the ion
entrance optics are formed by an einzel lens.
- 15 18. The device as claimed in claim 16 further including a
cold cathode field emission electron source provided in
front of the ion entrance optics.
19. The device as claimed in claim 16 further including an
20 electron source selected from one of:
a) a hot-cathode source,
b) a DC discharge source
c) an AC discharge source,
d) an electrospray source.
- 25 20. The device as claimed in claim 16 wherein a pair of RF
electrodes are placed in front of the ion entrance optics
in order to create a plasma.
- 30 21. The device as claimed in claim 16 wherein the ion
entrance optics are formed from an etched fluid channel
combined with a set of electrodes that together define an
electrospray source.
- 35 22. The device as claimed in any preceding claim wherein

each of the wafers are bonded silicon on insulator wafers.

23. The device as claimed in any preceding claim further
5 including two or more distinct chambers, the provision of
distinct chambers enabling the use of the device within a
differentially pumped system.
24. The device as claimed in any preceding claim further
10 including an ion source provided in a mesh configuration.
25. The device as claimed in any preceding claim wherein at
least some of the plurality of electrodes are arranged in
a mesh configuration.
15
26. The device as claimed in any one of claims 1 to 23
wherein at least some of the plurality of electrodes are
configured in a tube arrangement.
- 20 27. The device as claimed in claim 26 wherein the tube
arrangement provides a lens located at at least one of
the entrance or exit to the electrode rods.
28. The device as claimed in any preceding claim wherein at
25 least some of the plurality of electrodes are configured
as ion reflectors.
29. The device as claimed in claim 28 wherein the ion
reflectors are configured to provide a linear ion trap.
30
30. The device as claimed in any preceding claim further
including a filament element adapted to provide a source
of electrons, the filament element being configured as
one of the following types:
35 a) an externally provided filament,

- b) an integrally formed filament, or
- c) a removable filament.

31. A mass spectrometer system including a device as claimed
5 in claim 1 in combination with an ion source and/or an
ion detector, at least one of the ion source and/or ion
detector being provided externally to the device.

32. A mass spectrometer array comprising a plurality of
10 devices as claimed in any preceding claim.

33. A mass spectrometer system comprising two or more
devices as claimed in any one of claims 1 to 30, the two
or more devices being provided in series so as to form a
15 tandem mass spectrometer.

34. A mass spectrometer system as claimed in claim 33,
wherein each of the devices forming the series of devices
is a quadropole device and wherein a pair of RF
20 electrodes are placed between the cascaded quadrupole
devices in order to create a plasma.

35. A method of forming a mass spectrometer comprising the
steps of:

- a) etching an inner and outer pattern on a wafer,
the inner and outer patterns defining components
for the spectrometer,
 - b) bonding the wafer to a second wafer so as to form
a multilayer stack device,
 - c) inserting at least one electrode rod into the
device,
 - d) providing at least one electrode in the device
and,
- wherein the at least one electrode and at least one
35 electrode rod are provided on distinct layers of the

wafers.

36.A method as claimed in claim 35 wherein at least one of
the distinct layers is provided by an etching step
5 including at least two masks.

37.A method as claimed in claim 31 or 32 wherein the step
of providing the at least one electrode includes the
provision of the at least one electrode in at least one
10 of the following configurations:

- a) a tube arrangement,
- b) a mesh arrangement, and/or
- c) a diaphragm electrode arrangement.

15 38.A method as claimed in claim 37 wherein a mesh
arrangement is provided so as to define at least a
portion of a perimeter of a source cage into which
electrons may be injected from an external filament.

20 39.A method as claimed in claim 37 wherein the diaphragm
electrode arrangement is provided in the form of a three-
electrode configuration, inner and outer electrodes of
the three electrode configuration being configured to
operate at the same potential.

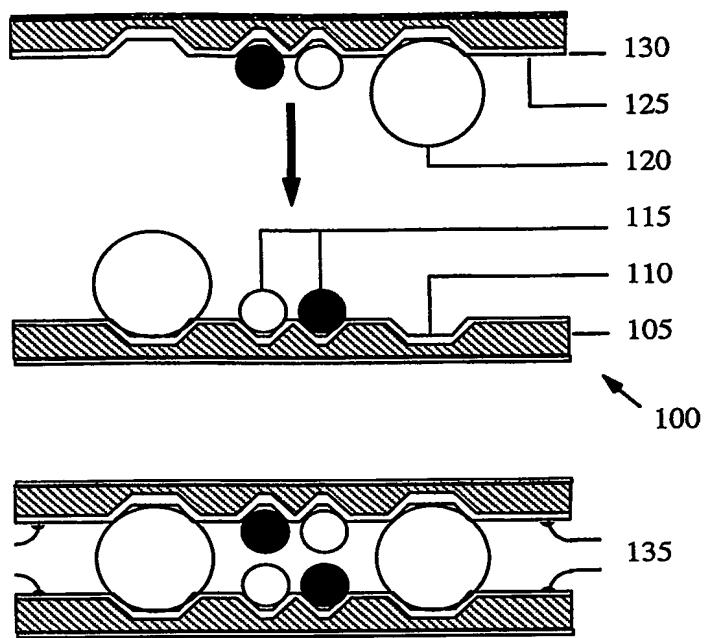
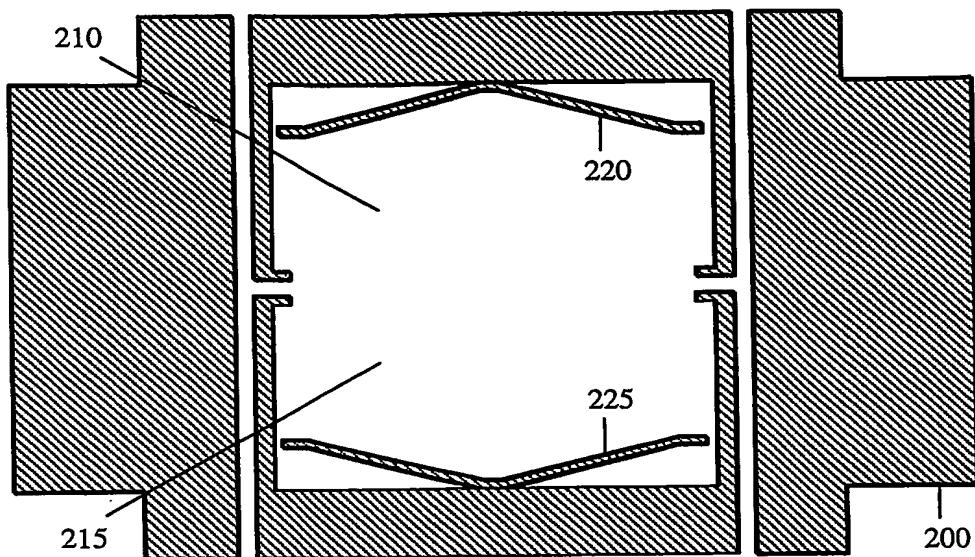
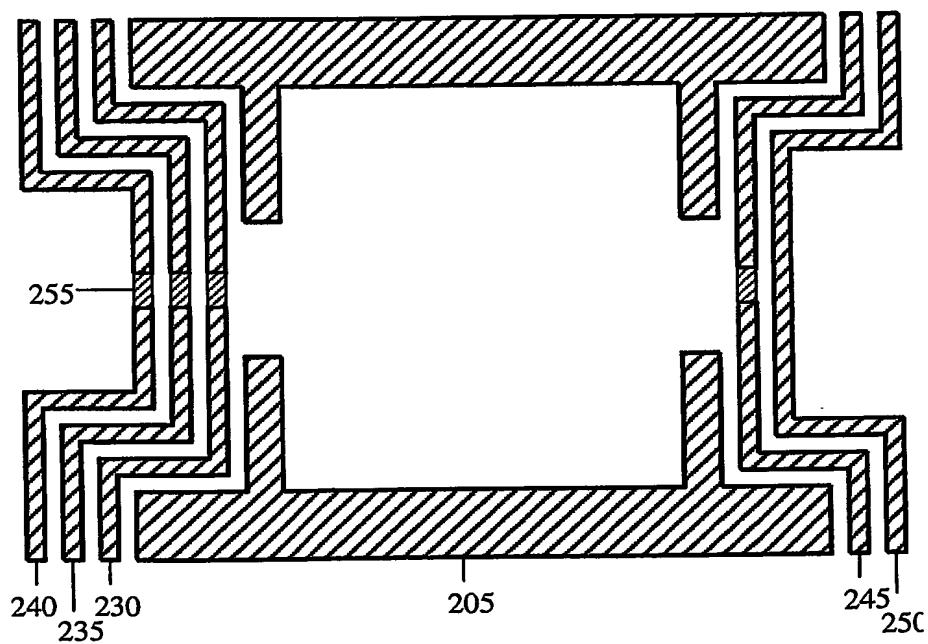


Figure 1.

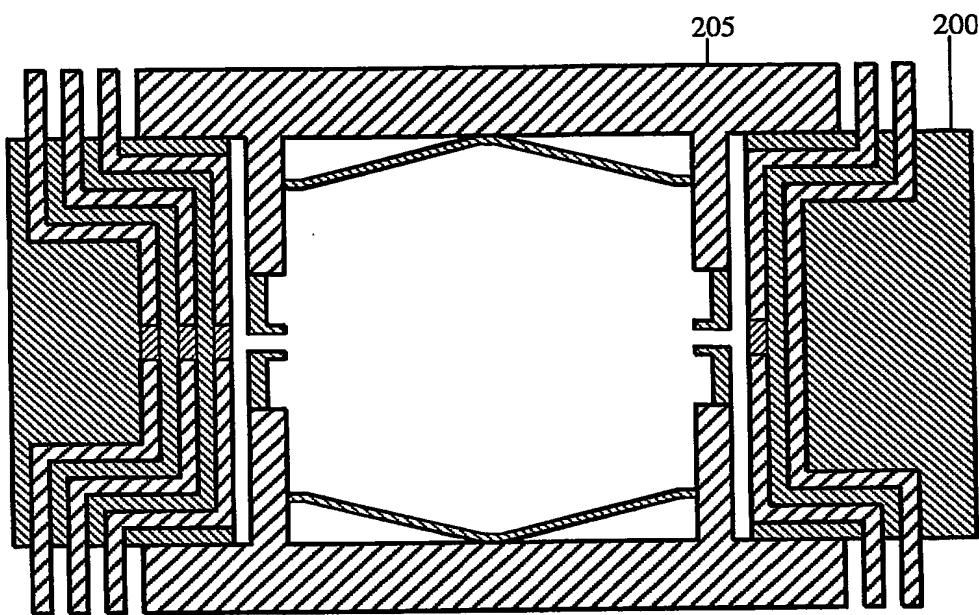


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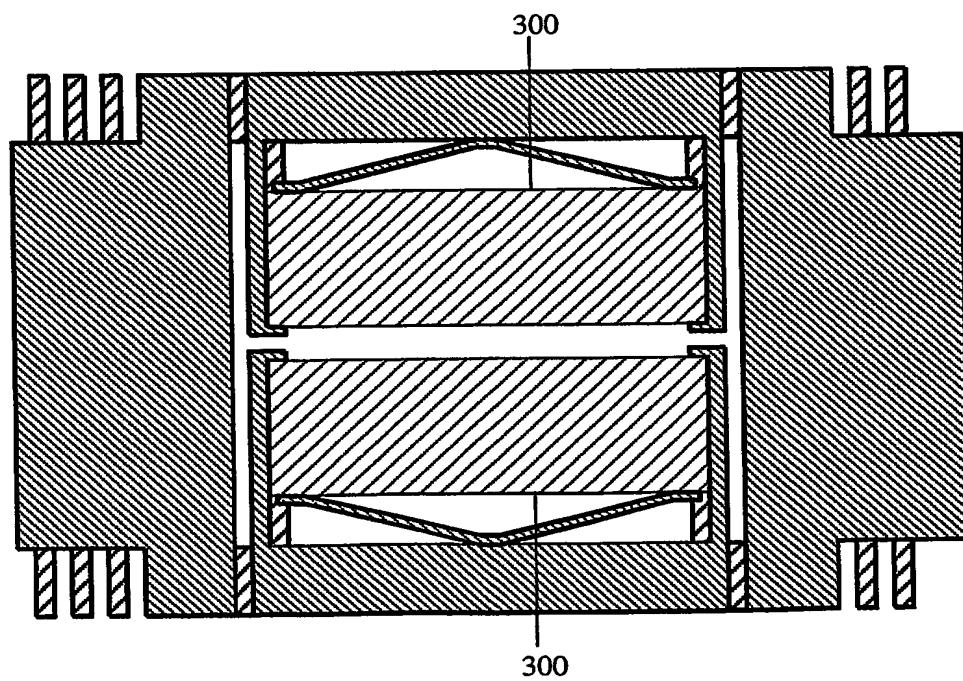


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Figure 2.

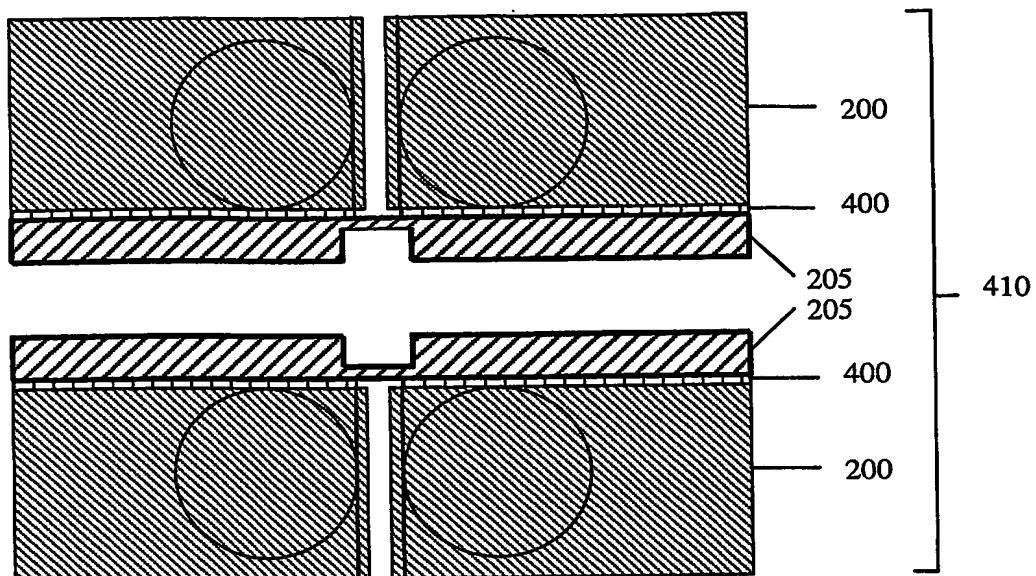


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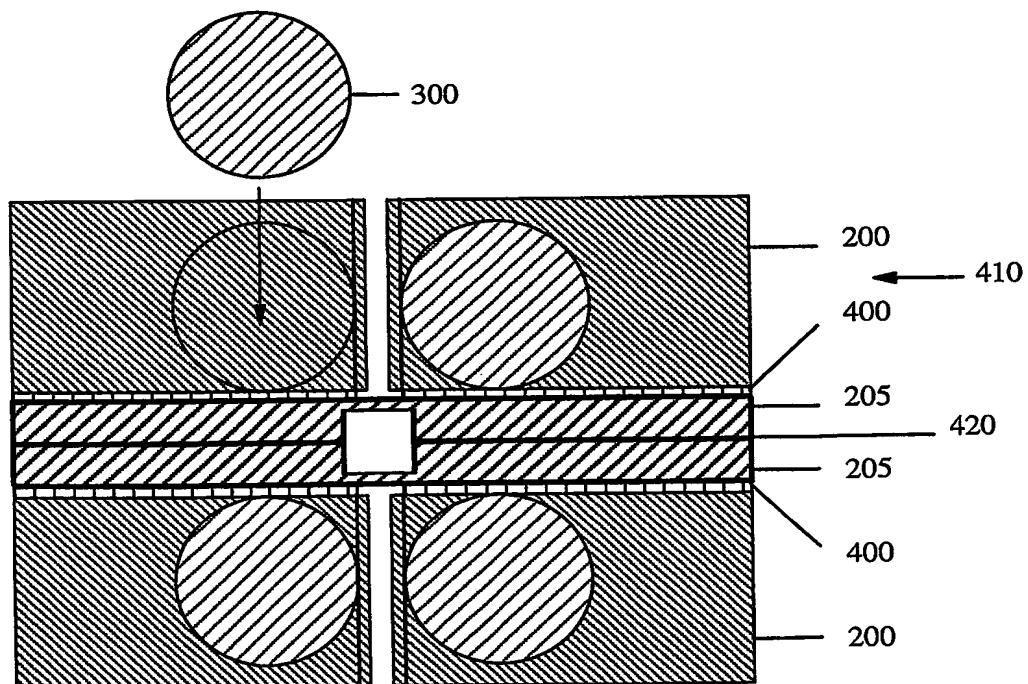


b)

Figure 3.



a)



b)

Figure 4.

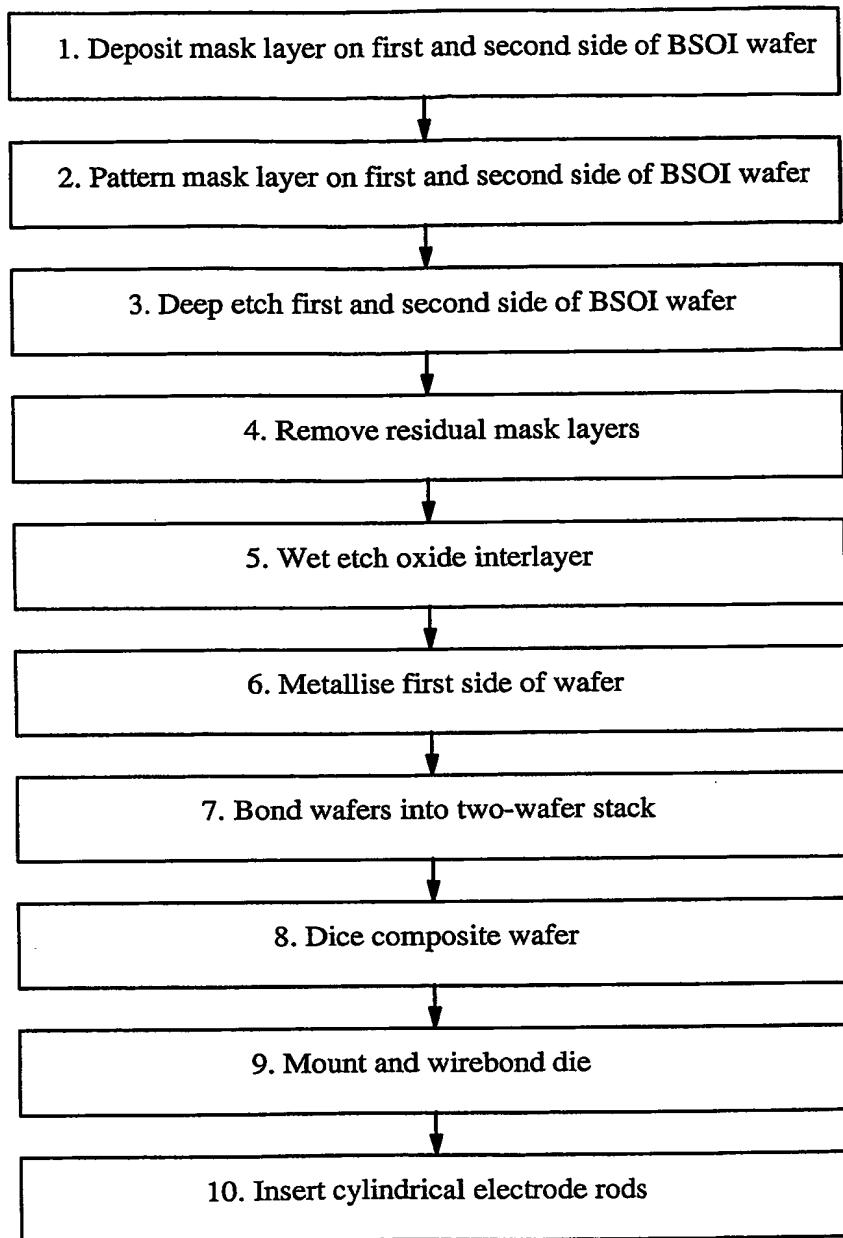


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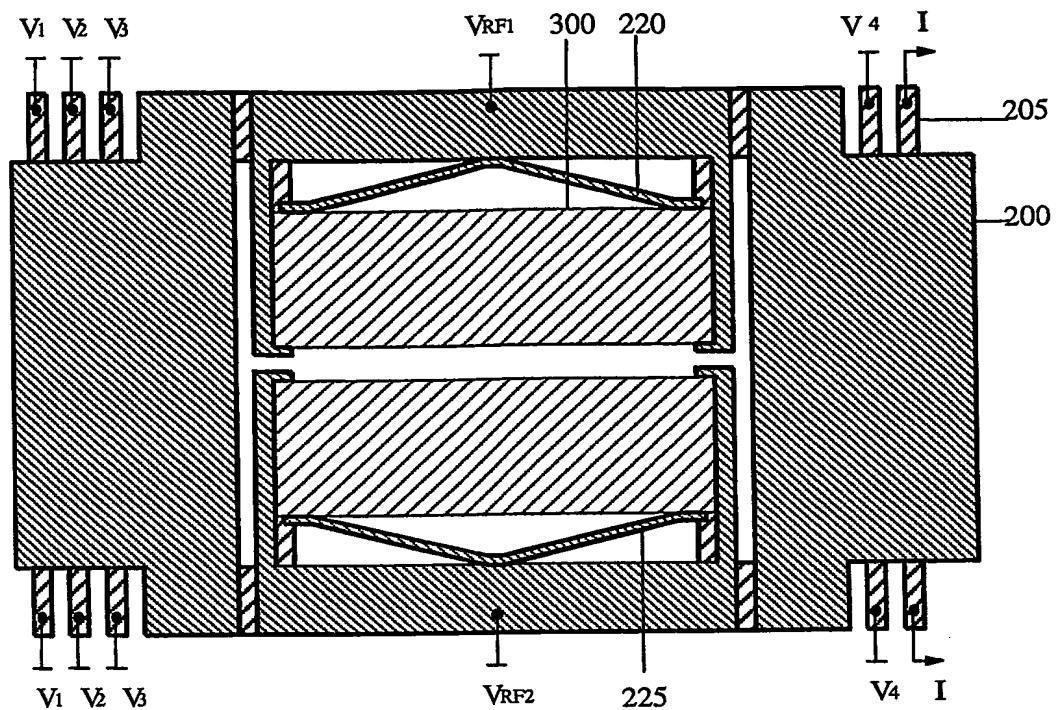
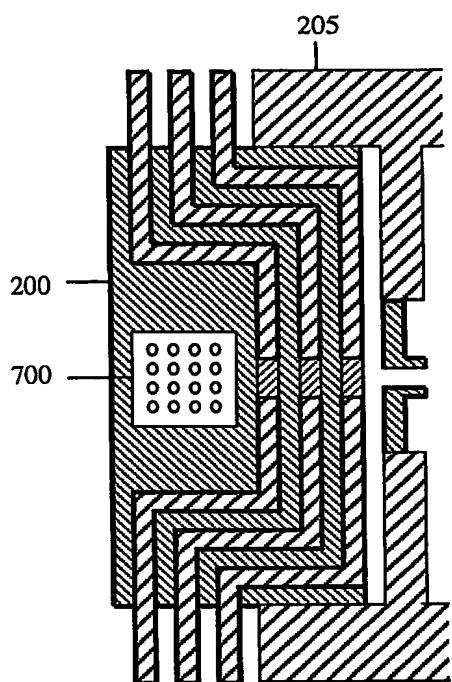
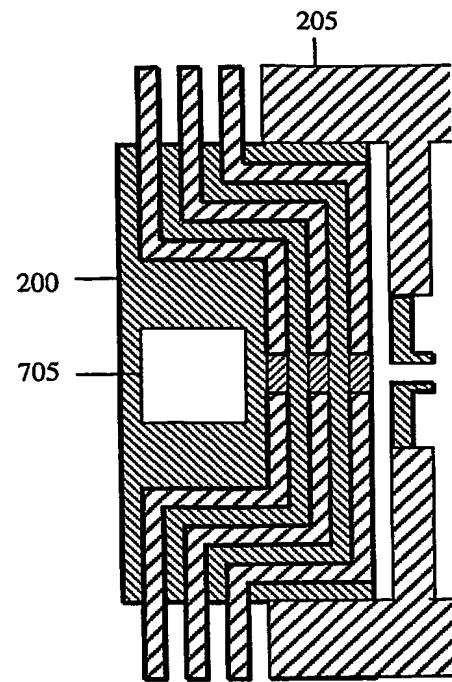


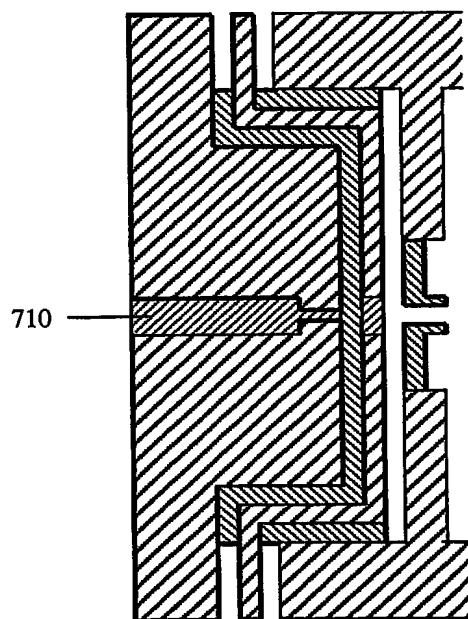
Figure 6.



a)



b)



c)

Figure 7.

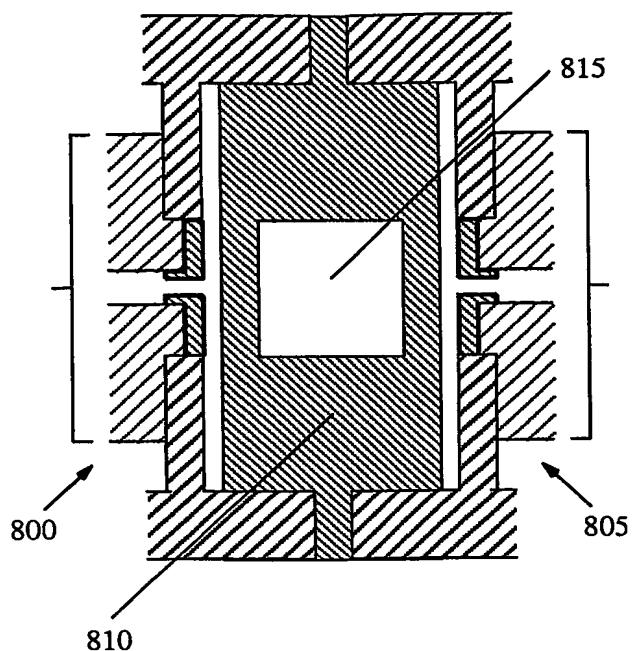
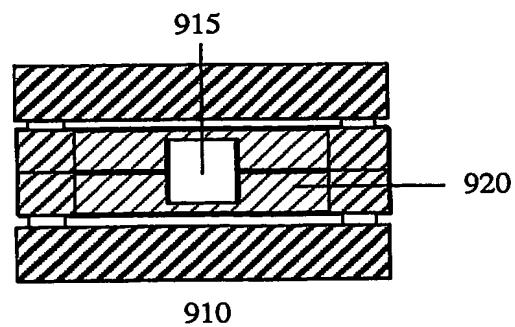
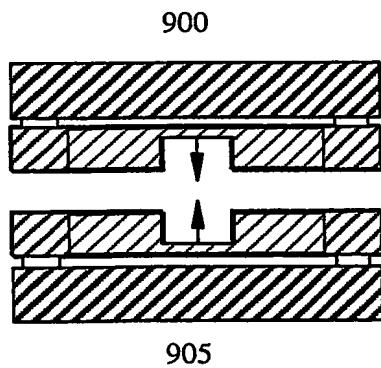
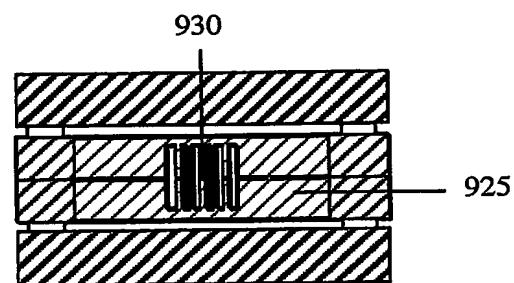
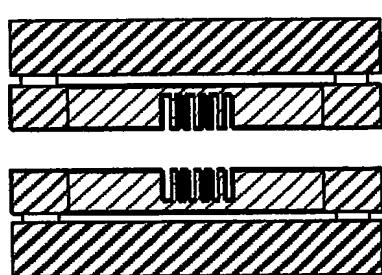


Figure 8.



a)



b)

Figure 9.

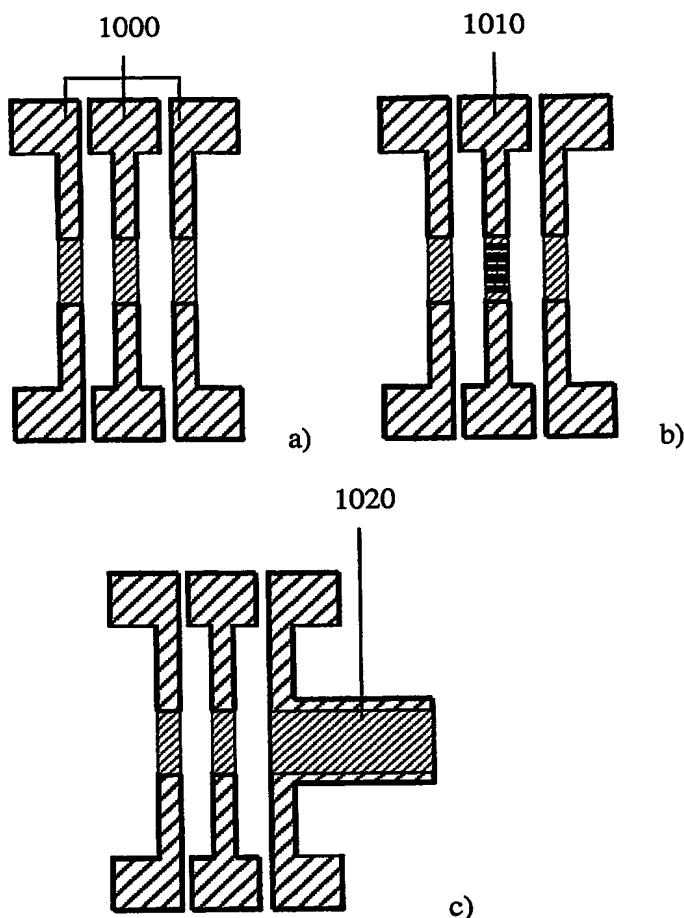
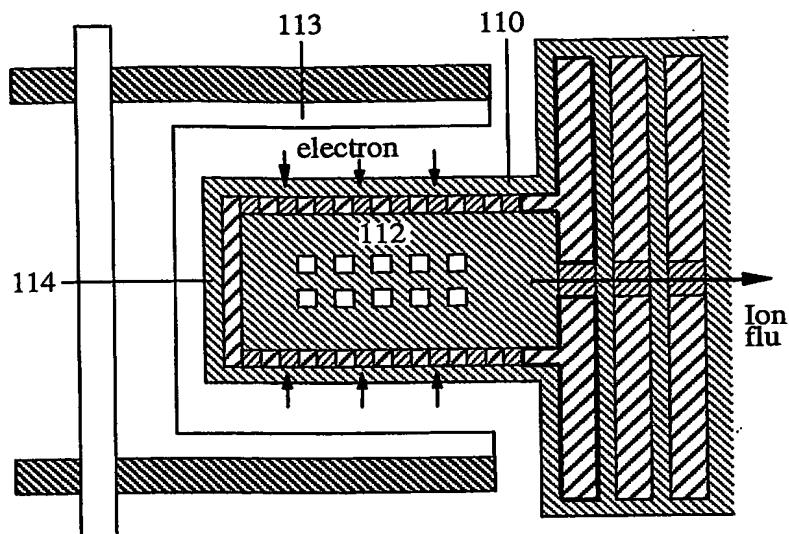
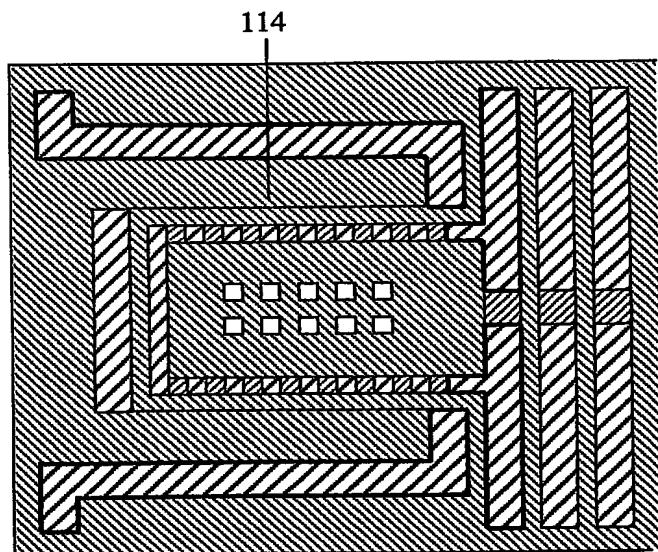


Figure 10.



a)



b)

Figure 11.